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Arnold M. Karo
Marc H. Mehlman
John R. Hardy

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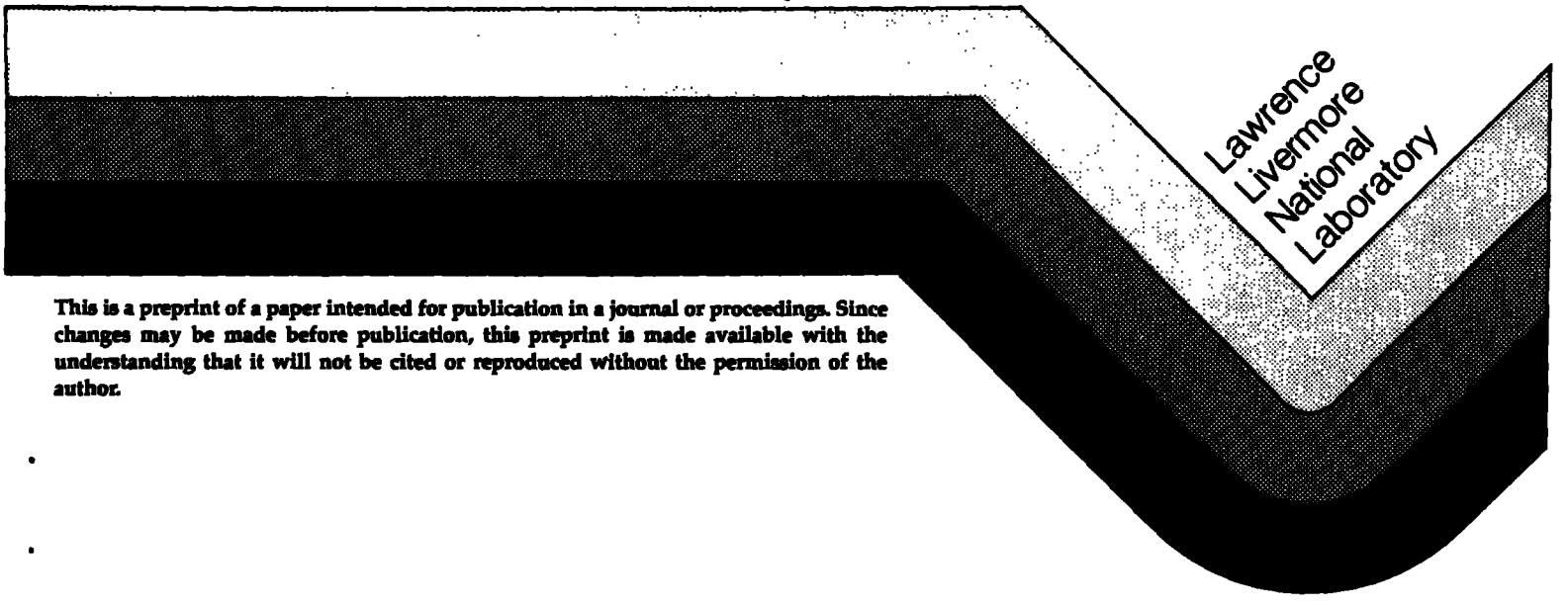

DISCLAIMER

THE DYNAMICS OF SHOCK-INDUCED ENERGY FLUX IN MOLECULAR BONDS*

Arnold M. Karo and Marc H. Mehlman
Lawrence Livermore National Laboratory
Livermore, California 94550

and

John R. Hardy
Behlen Laboratory of Physics, University of Nebraska
Lincoln, Nebraska 68577

Over the past ten years we have made many computer studies of shock propagation in condensed media. These studies employed the techniques of computer molecular dynamics (CMD), based on computer solutions of the classical equations of motion for the individual atoms in the condensed media. Recently, we have begun to re-evaluate the information obtained in order to achieve a flexible compromise between "brute force" averaging and continual monitoring of the detailed motion of the individual atoms. The method we have chosen is Fourier analysis in the temporal domain of the motions of groups of atoms which can be preselected.

Here, we present an analysis of our early canonical studies and of new data on disordered systems. The present work also utilizes our current codes which contain "neighborhood look-up" procedures designed to examine the system at regular intervals and to determine which bonds should be retained, removed, or added as the system rearranges under shock loading.

INTRODUCTION

It is now well-established that computer molecular dynamics (CMD) can provide a unique insight into the behavior of shocked systems which, at present, is inaccessible to direct experimental investigation (1,2). The basic reason is that CMD studies show that shock fronts are characterized by violent local structure at the atomic and molecular levels, which varies drastically over time scales of picosecond to femtosecond duration. Since present experimental studies typically examine a system over nanosecond or greater time intervals and in micrometer dimensions, it follows that they will monitor spatial and temporal average behavior rather than the true local behavior. While it is true that experiments have been done with considerably shorter scales of time or distance, none has yet been done where <u>both</u> scales have been shortened simultaneously. However, recent studies on shocks in water (3) represent major steps towards this goal.

Since presenting our first work (1) on CMD at the Sixth International Colloquium on Gasdynamics of Explosions and Reactive Systems, we have carried out many studies with the aim of achieving an increasingly accurate description of reality (2,4). Most recently we have concentrated on developing techniques for post-processing of the raw CMD data, with the principal aim of achieving some optimum capability, which will combine reasonable compactness with the retention of the maximum amount of information about the CMD history of each shock study. From the outset we have stressed the importance of avoiding the wholesale destruction of information (obtained at a non-trivial expense in computer time) that is inherent in the formation of broad averages over many atoms and/or long time intervals. Moreover, this destruction is no longer necessary with contemporary computer facilities; since it is now possible to carry out a virtually unlimited number of post processing operations at a fixed cost by the use of a dedicated microcomputer, it is no longer

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necessary to use mainframe computer time to perform such studies.

Given these facts, it seemed logical to begin by monitoring local variables, such as energy, as a function of time for a selected unit. In this manner we could observe the manner in which energy flowed into and out of this unit and, in the case of a polyatomic unit, the energy flux between different degrees of freedom. Then, by enlarging our unit, we could progressively monitor increasingly less local conditions if this appeared desirable. We have recently reported the earliest of our findings (5,6) employing this approach and demonstrated its potential usefulness. However, it was also evident that further compacting of the data was desirable, and the most promising approach was to compute their temporal Fourier transforms. This can be done for varying time intervals, provided they are not too short (a circumstance that we wish to avoid in any event if we are to achieve any useful compacting of the data), and the whole history thus reduced to a manageable number of figures.

This additional capability, together with the greatly increased sophistication of our CMD codes, has made it desirable that we repeat a selected set of our earlier calculations, which we regard as canonical; in addition, we have added some completely novel investigations which address new areas not previously explored.

Thus, in the present paper, we focus on studies of diatomic systems (which have earlier only been reported in summary form), which are important in their own right as the first step to the truly polyatomic systems represented by organic explosives and binders and which also lead naturally to the introduction of the simplest possible type of disorder in a controlled fashion. This comes about because if one introduces only mass disorder by inserting in a random fashion "wrong" masses in a monatomic host, then one is introducing both position and mass disorder simultaneously. However, if one begins from a regular diatomic host and replaces atoms of one sub-lattice by atoms of the other sub-lattice species, but retains an ordered array for the other sublattice, one is introducing only mass disorder.

SPECIFIC STUDIES

The techniques of CMD are now well documented by both others and ourselves (2,7). The only novel features are the use of "look-up" procedures to keep track of the interatomic bonding and the various post processing options referred to in the Introduction. In the present rather preliminary account, our basic objective is to "revisit" some of our earlier studies with the aid of these new techniques. As before, for reasons of computational economy, these studies have been primarily restricted to two-dimensional systems.

DIATOMIC STUDIES

We begin by reporting the results of two runs on regular diatomic lattices, subject to loading by impact of a plate composed entirely of heavy atoms (= 10 amu). They differ only in the nature of the column of atoms which the plate initially strikes: in the first case, it is composed of heavy atoms (= 10 amu), in the second case, it is composed of light atoms (= 1 amu).

In Figs. 1 and 2, we show a sequence of stills from the movie history of the first case (heavy on heavy) designed to reveal the overall history of this system. Evidently there is considerable lattice disruption which is both coherent and athermal. The behavior of the last spalled fragment on the right is particularly interesting, since it appears to evolve in a manner revealing considerable shock-induced (athermal) chemistry, involving rupture and subsequent "healing" of a number of bonds.

In Figs. 3 and 4, we show a similar sequence of stills from the history of the lattice with light atoms forming the initial column on the left. (Since the choice of such

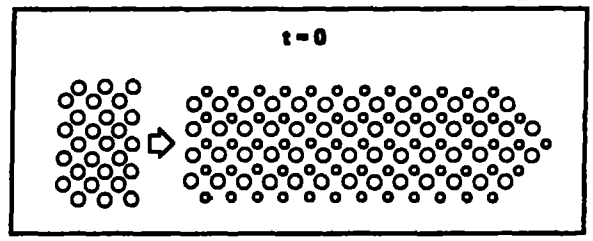

Figure 1. Initial configuration for a diatomic lattice (masses = 1 and 10 amu) shock loaded by impact by a monatomic (mass 10) plate: plate striking column of mass 10 atoms. Smaller and larger circles designate mass 1 and mass 10 atoms, respectively.

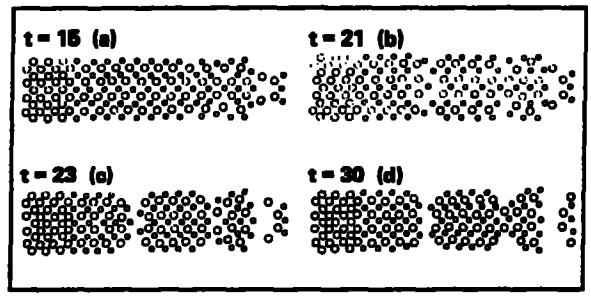

Figure 2. Configurations of the diatomic system of Fig. 1 at various times (in units of 10^{-14} s). Smaller and larger circles designate mass 1 and mass 10 atoms, respectively. a) t = 15. b) t = 20. c) t = 23. d) t = 30

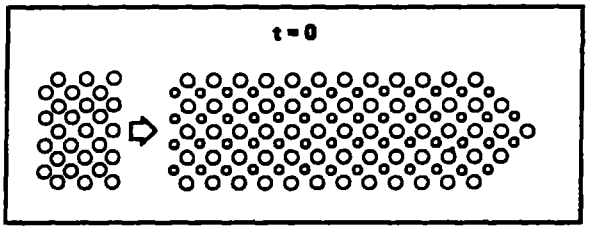

Figure 3. Initial configuration for a diatomic lattice (masses = 1 and 10 amu) shock loaded by impact by a monatomic (mass 10) plate: plate striking column of mass 1 atoms. Smaller and larger circles designate mass 1 and mass 10 atoms, respectively.

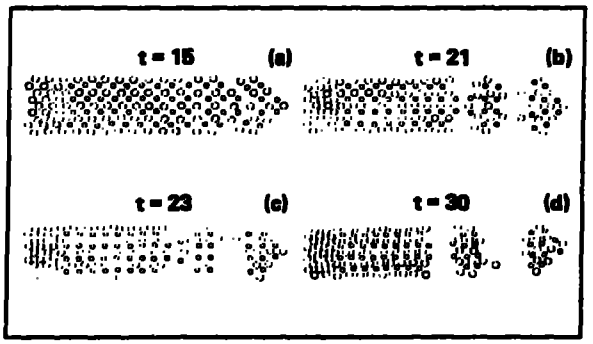

Figure 4. Configurations for the diatomic system of Fig. 3 at later times (in units of 10^{-14} s). a) t = 15. b) t = 21. c) t = 23. d) t = 30. Smaller and larger circles designate mass 1 and mass 10 atoms, respectively.

stills is determined by the history itself, the selected times are not necessarily the same for every run.) It can be seen that the "rupture pattern" is very different from that of the previous run. Apparently the somewhat less "impulsive" shock loading due to the "indirect" (light-atom-mediated) impact, rather than the direct impact of heavy plate atoms on heavy lattice atoms, has favored the spall of larger more coherent lattice fragments; additionally, the high degree of local activity at the pointed end is no longer present.

In order to exploit our new post processing techniques, we Fourier transformed the energy of a pair of near-identically situated light and heavy atoms for both histories. We did this by dividing the thirty-time unit history into three blocks of ten units (one time unit = 10^{-14} s). The resultant transforms are shown in Figs. 5 and 6. Probably since the atom pairs are located within the coherent lattice fragments, the transforms show no very dramatic features, but the data reduction is very promising, and further study is indicated.

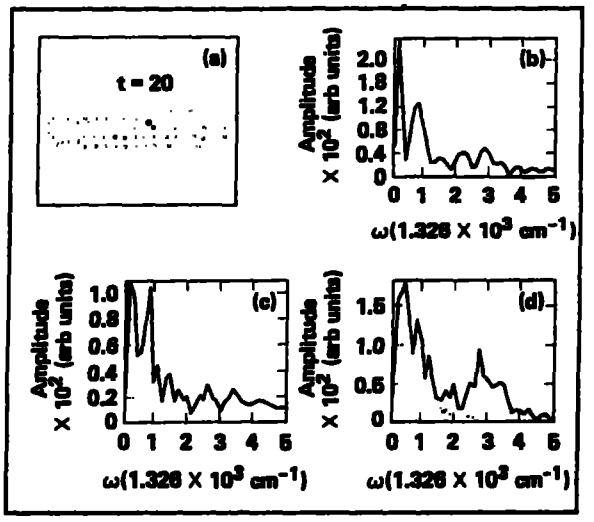

Figure 5. Fast Fourier transforms for the vibrational energy of a single diatom (masses 10 and 1) in a diatomic lattice shock loaded by a heavy plate (mass 10 atoms) initially striking column of mass 10 atoms (units of time in 10^{-14} s). a) Configuration at t = 20 showing tagged diatom, indicated by filled circles. Light masses shown as smaller circles. b) FFT, t = 0-10. c) FFT, t = 10-20. d) FFT, t = 20-30.

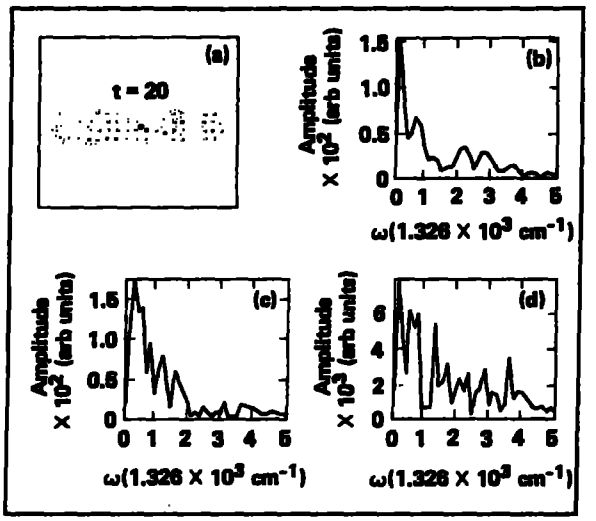

Figure 6. The same sequence as Fig. 5 except that the plate strikes a light column and the tagged diatom is somewhat differently situated (units of time in 10^{-14} s). a) Configuration at t = 20 showing tagged diatom indicated by filled circles. Light masses shown as smaller circles. b) FFT, t = 0-10. c) FFT, t = 10-20. d) FFT, t = 20-30.

DISORDERED SYSTEMS

In order to characterize the effects of disorder, we set up three diatomic systems identical to the first set of studies described above (Figs. 1 and 2), except that the lattices have been disordered on the "light atom" sublattices by random replacement of ∿45%, 67%, and 84%, respectively, of the light masses by heavy atoms. Selected stills from the history of the 67% case are shown in Fig. 7.

The most striking effect is the almost complete suppression of the atomically sharp shock front found in the ordered systems. This is most clearly manifested by the disappearance of spall and a general tendency for the coherent shock energy to degrade into quasi-random atomic motion leading to "quasi-melting" (semi-random emission of fragments).

In order to quantify this behavior, we again performed Fourier transform post processing for a pair of atoms situated in near proximity to the position of the pair selected in the first study (a heavy plate impacting a diatomic lattice in which the first column is composed of heavy atoms). The results are shown in Fig. 8.

In all cases it is of interest to observe the amount of energy delivered to the diatomic unit whose history is being studied, and to compare this with the bond rupture energy, in order to determine whether bond rupture would be possible at some local surface (bond rupture in the bulk of the lattice is precluded by the caging effect of the neighboring atoms). In all three studies it appears that surface bond breaking is indeed the case even though (except in the disordered systems) the actual lattice

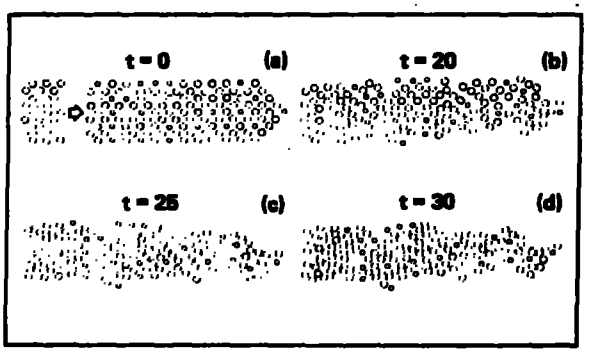

Figure 7. a) Initial configuration for a diatomic (masses = 1 and 10 amu) lattice disordered on the light sublattice by random replacement of ∿67% of the light masses by mass 10 atoms. Smaller circles designate mass 1 atoms. History of the disordered lattice at later times (in units of 10^{-14} s). b) t = 20. c) t = 25. d) t = 30.

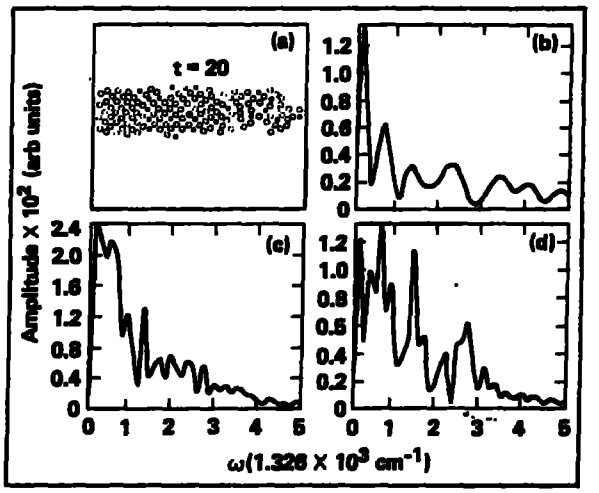

Figure 8. Fast Fourier transforms of the vibrational energy of a diatom in the disordered lattice during the simulation shown in Fig. 7. a) Configuration at t = 20 showing the tagged diatom, indicated by filled circles. Light masses shown as smaller circles. b) FFT, t = 0-10. c) FFT, t = 10-20. d) FFT, t = 20-30. The additional "spike" in the t = 20-30 transform at a frequency ∿ 1.5 (∿1990 cm^{-1}) is probably the "pumping" of energy into the tagged pair by the motion of the heavy atom first neighbor of the tagged heavy atom.

"temperature" is quite low--the principal reason for this apparent paradox is that bond rupture at a surface is an irreversible process which is likely to occur whenever the instantaneous bond energy exceeds the bond rupture energy. Thus, while in the bulk, energy flows coherently into and out of bonds as the shock transits the lattice and, after the passage of the front, the average bond energy reverts essentially to its value prior to the shock incidence, at the surface/void the instantaneous bond extension can exceed the bond energy and readily produce rupture, or monomolecular decomposition. Hence, by this means are formed atomic (ionic/radical) fragments of high reactivity which can initiate a propagating chemical reaction when produced in sufficiently large concentrations. In Fig. 9, we show a comparison of the vibrational energies of the diatoms chosen for the ordered diatomic lattice and the disordered diatomic lattice (Figs. 5 and 8).

One additional feature is that examination of energy propagation through the light and heavy sub-lattices reveals that propagation occurs primarily through the heavy sub-lattice. This is consistent with the partition of energy between the center-of-mass (CM) and internal motion of each diatomic unit. The internal (within the CM system) motion, by definition,

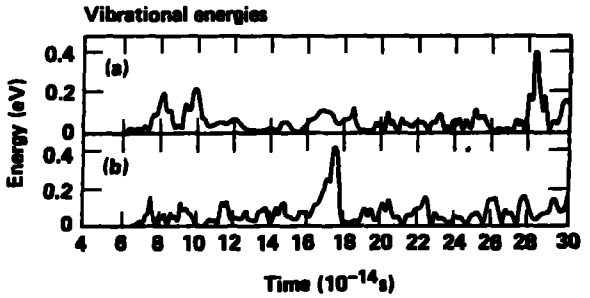

Figure 9. Comparison of the vibrational energies of the corresponding diatoms in the ordered diatomic lattice, Fig. 5, and the disordered diatomic lattice, Fig. 8.

has no net momentum, thus momentum propagation is confined entirely to the overall CM motion and, for widely disparate masses, is primarily carried by the heavier atom.

This is a somewhat simplified picture since, at first sight, it would seem to imply that energy never reaches the internal motion, at least not beyond the first pair of columns. However, a little closer examination of the problem reveals that this is incorrect. The impact of a neighboring pair of shocked columns on their unshocked forward neighbors is a more complex process because the pairs do not strike one another as hard rods; rather, the heavy members of the moving pair push directly only against the light column of the unshocked pair. Thus, initially, they effectively push the light column before them without resistance. However, as this process compresses the initially unshocked columns, the bonds between them become more and more rigid, until the heavy column has assumed the bulk of the CM motion of the impacting pair of columns. At this point the shock front has effectively jumped one pair of columns and the transfer of energy is complete, including the transfer of energy to the internal motion (light atom beating against heavy atom) within the CM system. This is an important point, possibly crucial, because it implies that the internal motion will be drastically athermal due both to the coherent and rapid nature of the energy transfer during a time $\sim$ 10-100 femtosecs. Hence, arise the bond ruptures at surfaces and other imperfections that we observe in our simulations (1,2).

CONCLUSIONS

We have presented results demonstrating the potential usefulness of post-processing Fourier transforms as a means of "fingerprinting" the nature of shock loading in a variety of situations. The one single common feature is that these transforms again show that shock loading can excite high frequency intramolecular motions over picosecond time intervals in a strongly athermal manner. The transforms, themselves, although not particularly dramatic for these selected studies, do reveal a high degree of promise as a data reduction scheme which drastically reduces the amount of output while retaining all, or almost all, of the important microscopic information.

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